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CSIRO In-Situ Lab: A multi-pronged approach to surface gas and groundwater monitoring at geological CO_2 storage sites

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ABSTRACT

In February 2019, at the CSIRO In-Situ Laboratory CCS project, a test was conducted where 38 t of gaseous CO_2 were injected over 5 days into a fault zone at a depth of approximately 340 m. As a release test, this project enabled the testing and validation of surface and shallow well monitoring strategies at intermediate depths (i.e. depths much deeper than previous release projects and shallower than reservoirs used for CO_2 storage). One of the aims of this project is to understand how CO_2 would behave at intermediate depths if it did migrate from deeper depths (i.e. from a storage reservoir); the CO_2 was not intended to migrate to the shallow subsurface or to surface/atmosphere. To verify that the injected CO_2 remained in the subsurface, and to comply with environmental performance requirements on site, a comprehensive surface gas and groundwater monitoring program was conducted. The monitoring strategy was designed such that any leakage(s) to the surface of injected CO_2 would be detected, mapped and, ultimately, quantified. The surface air monitoring program was comprised of three different but complementary approaches allowing data to be efficiently collected over different spatial and temporal scales. These approaches included continuous soil-gas chamber measurements at fixed locations, periodic soil-gas chamber measurements on gridded locations and near-surface atmospheric measurements on a mobile platform. The surface air monitoring approaches gave self-consistent results and reduced the risk of "false negative" test results. The only anomalous CO_2 detected at the surface flowed from the observation well and could be directly attributed to a breach in the well casing at the injection depth providing a conduit for CO_2/water to rise to the surface. Groundwater monitoring program revealed no impact on the groundwater resources attributable to the carbon injection project. Based on this work, we demonstrate that this multi-pronged monitoring strategy can be utilized to minimize the overall resources devoted to monitoring by increasing the number of monitoring approaches and diminishing the resources devoted to each technique. By maximizing the effectiveness of each element of the monitoring program, a cost-efficient and robust monitoring strategy capable of early leak detection and attribution of any leaking CO_2 can be achieved.

1. Introduction

Globally, there have been 16 subsurface CO_2 release experiments established (Roberts and Stalker, 2017) such as the ZERT project in Montana, USA (Strazisar et al., 2009), Ginninderra release site near Canberra, Australia (Feitz et al., 2018a) and the offshore QICS project in the UK (Blackford et al., 2015). These projects have provided opportunities to optimize and validate a wide range of surface gas and groundwater monitoring methodologies and technologies. Studies of artificial seeps complement research at natural analogues for CO_2 seepage because at release experiments the exact quantity of CO_2 injected is known, unlike natural analogues (Schutze et al., 2012), enabling a fuller understanding of CO_2 fate and leak rates.

Studies of natural analogues find that geological faults pose the greatest risk of CO_2 leakage to surface from deep geological reservoirs (Miocic et al., 2016). However, fault zones are complex and

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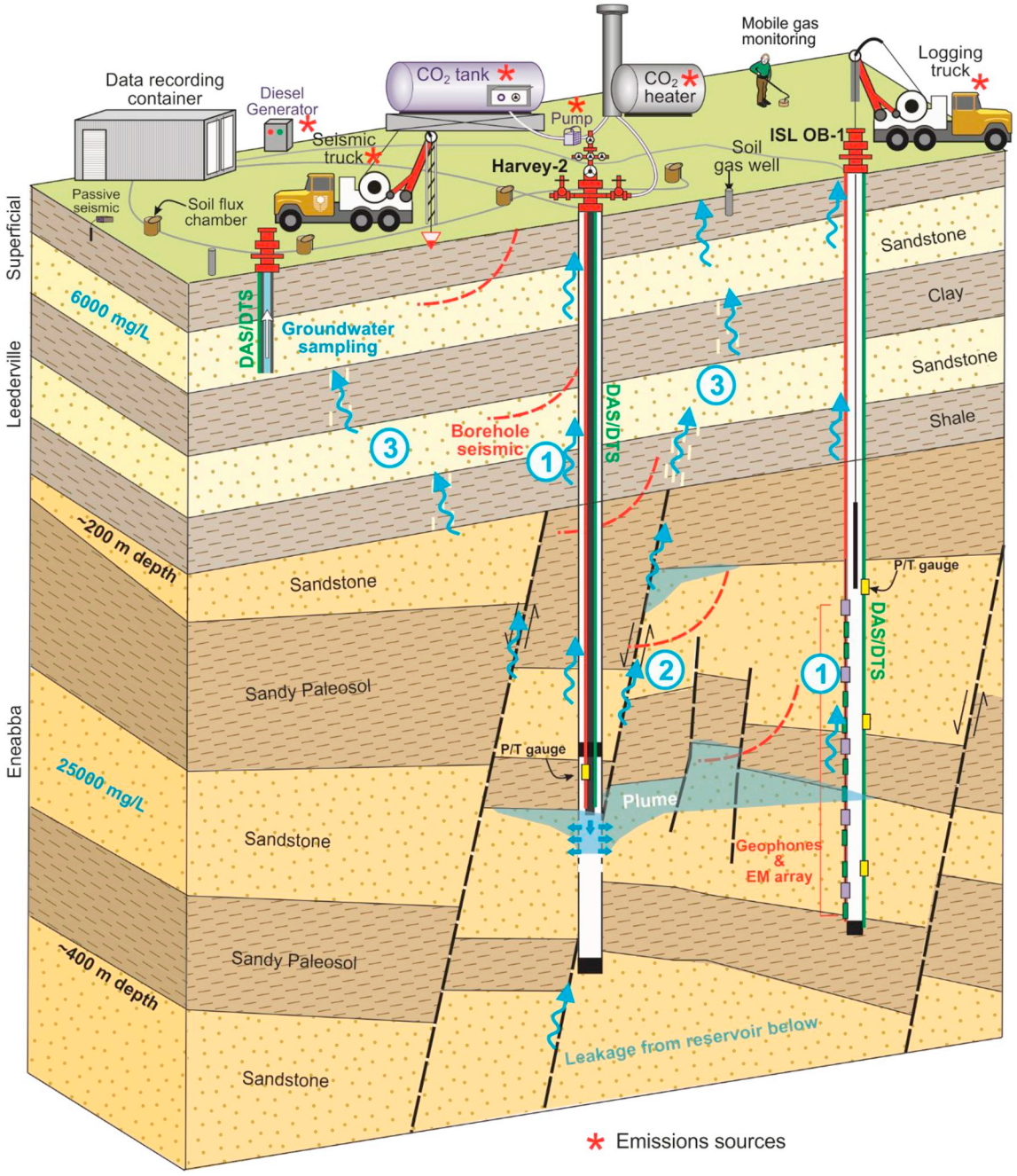

Fig. 1. Concept of In-Situ Laboratory for monitoring CO_2 leakage processes. Injection of CO_2 mimics a secondary CO_2 accumulation due to leakage from a deep reservoir. Potential leakage processes to the ground surface include: 1) leakage along well due to inadequate cementing, 2) leakage along faults and 3) leakage through zones of weakness in sealing units. Potential emissions sources at the ground surface are identified by a red asterisk. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

heterogenous, and how they influence fluid flow can be highly variable (Fairley and Hinds, 2004; Wibberley and Shipton, 2010) As such, there is significant interest in understanding the impacts of faults on subsurface storage and potential migration pathways (Shukla et al., 2010). The natural analogue in Latera caldera in Italy provides an opportunity for understand migration in a fault zone (Annunziatellis et al., 2008). In this instance, the narrow spatial characteristics of leaking CO_2 on the surface suggest that the migration pathway to the surface is only along high permeability fractures. The EU-funded ENOS program intends to inject CO_2 into a faulted limestone/basalt reservoir at 250 m depth as part of activities within the Sotacarbo Fault Laboratory (SFL) in Italy (Bigi et al., 2017). This project aims to test the sensitivity and effectiveness of tools designed to monitor potential gas leakage and understand changes in groundwater quality (if CO_2 enters the aquifer). CO_2 injection into a shallow fault zone is also planned at the CO2CRC Otway Basin at a depth of approximately 30 m (Feitz et al., 2018b). However, prior to this project, in which CO_2 was injected at a depth of approximately 340 m in early 2019, no field experiments had been undertaken to release CO_2 into or close to geological faults in the subsurface. The In-Situ Lab project is therefore the first project of its kind.

2. In-Situ Laboratory project site geology and aquifers

The In-Situ Laboratory project site is a greenfield investigation site located south of Perth, Western Australia and is part of the South West

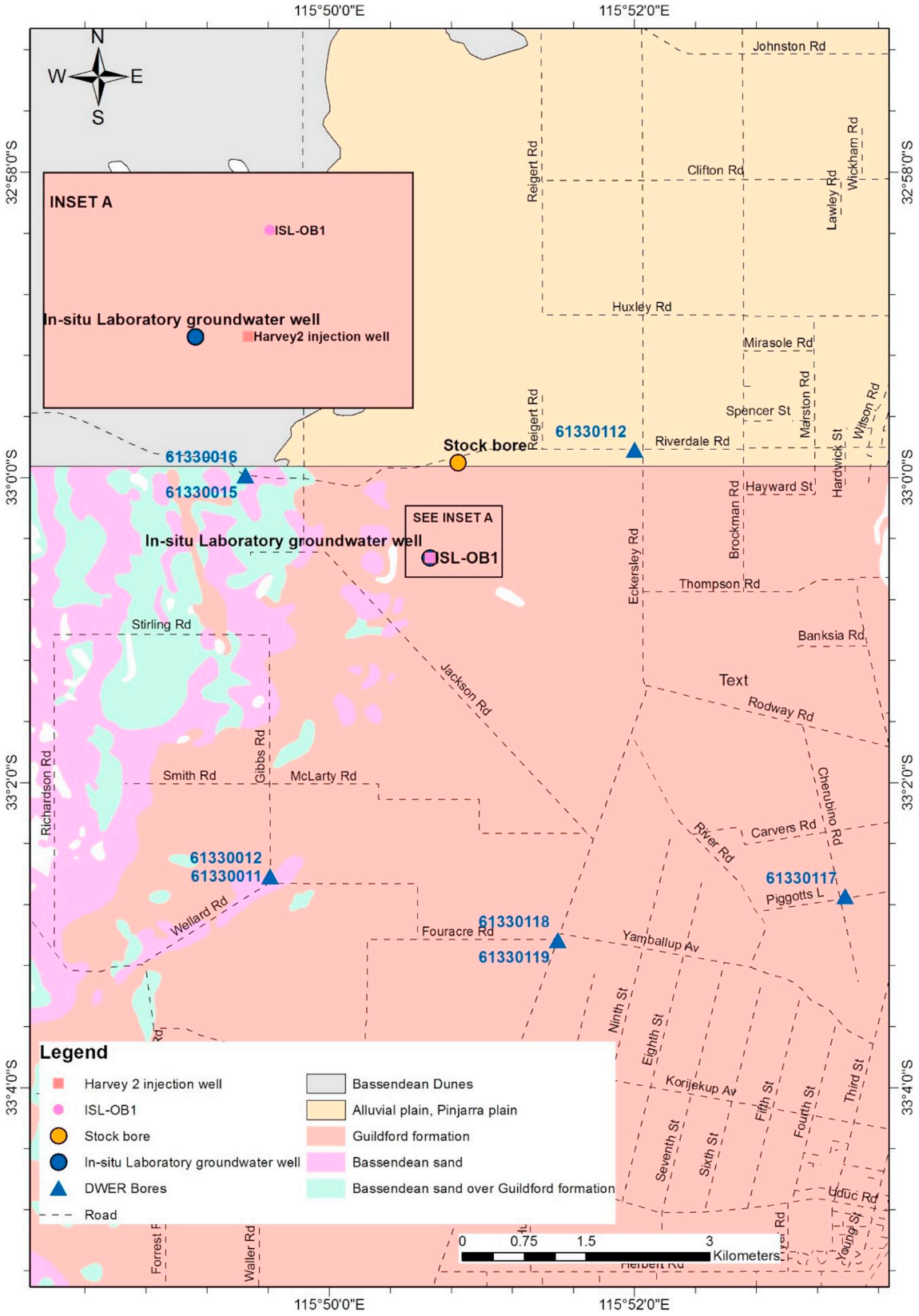

Fig. 2. Location of groundwater and monitoring wells.

Hub project area (Karsten Michael et al., 2019). The site is located within the Harvey Ridge structural subdivision of the Perth Basin. The Perth Basin is a sedimentary basin filled with sedimentary rocks, mainly sands and clays, laid down between the Permian and Cretaceous geological periods (300 to 100 million years ago), and is separated from the Archaean granitic rocks to the east by the Darling Fault (Commander, 2013). As seen in Fig. 1, at the site, there are thick interlayers of sandstone and shale with the upmost layer being a thick

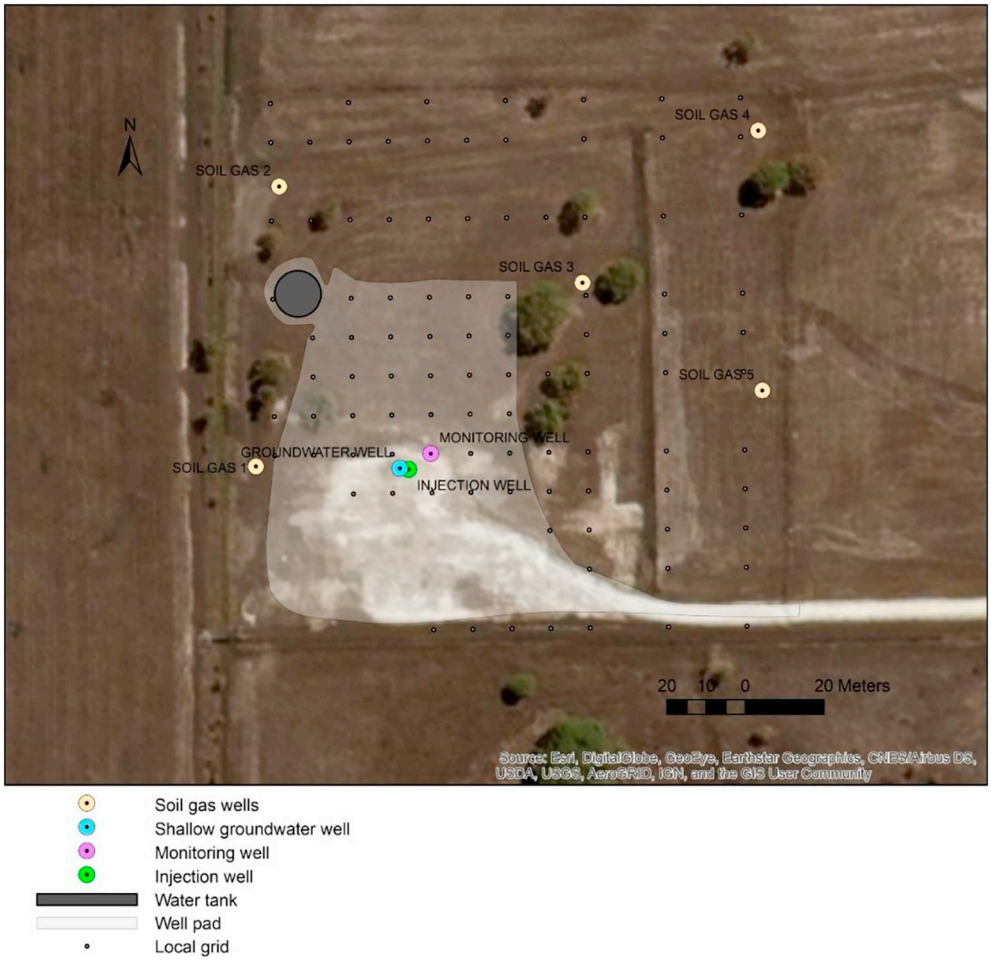

Fig. 3. Map of the CSIRO In-Situ Laboratory showing the location of the various wells, survey points and soil-gas sampling points on site.

Table 1
Summary of the surface monitoring that has been undertaken at the Harvey 2 site.

Method	Details	Frequency	Number of measurements
Fixed-site soil-gas flux: Licor Li-8100A and Los Gatos Research UGGA gas analyzers with an Li-8150 multiplexer and Li-8100-104 soil-gas chambers	Static system that is permanently mounted and solar powered. Comprises four chambers for determining the CO_2 flux (Fig. 4). Three of these are setup in the vicinity of the injection and observations well: one next to the injection well; one next to the monitoring well; one between the injection and monitoring wells. The fourth chamber is set up as a control further away from the wells on the western side of the site.	Data collected every 1 h for each chamber. One chamber measurement takes 15 min and cycles between the four chambers. Measurements are made continuously	Over 5200 data points
Soil-gas flux at gridded locations: West Systems	Portable and battery powered system (Fig. 5). Comprises a Li-COR 840A analyser and a chamber for measuring the CO_2 flux. Survey is made over a 40 × 40 m grid.	Twelve surveys have been conducted. Seven surveys before, two during and three after injection	Over 366 data points
Near-surface atmospheric concentration: Picarro G2201-i CRDS	Mobile system that measures the CO_2 and CH_4 concentration in the atmosphere about 10 cm above the ground. The system is powered by lithium ion batteries and mounted on a trolley that is manually moved around the site. Comprises GPS to track location (Fig. 6).	Fifteen surveys were conducted. Data collected every second and in real-time	Over 30,000 data points
Soil-gas wells	Installed five soil-gas tubes at a depth of 1 m around the north part of the site. Consists of a 20 cm stainless steel screen and Teflon tubing to the surface. The gas wells were sealed with bentonite and gas samples collected into a Calibond-5 bag via a syringe (Fig. 7).	Two before, two during and one after injection	19 samples

Fig. 4. Li-COR setup for monitoring the soil-gas flux on the crushed limestone well pad.

Fig. 5. West Systems setup for monitoring CO_2 soil-gas flux used on the grid patterns in Fig. 3.

clay layer.

The groundwater bores monitored for this study are located between towns of the Uduc (located south west of the site) and Cookernup (located north east of the site) and all lie within a 1 km radius of the injection well. Groundwater use in the SW Hub project area is generally restricted to shallow bores in the superficial aquifer as most of the groundwater in the underlying confined aquifers is brackish or saline. The major aquifers at the In-Situ Laboratory project site are the Perth Superficial, Leederville and Eneabba aquifers (Fig. 1). The presence of water resources means that there is strong community interest in demonstrating the ongoing integrity of water resources in parallel with CO_2 storage (Caritat et al., 2013).

2.1. Perth Superficial aquifer

The Superficial Aquifer Formations consists of Quaternary and Late Tertiary sediments which extend from the Darling Scarp to the coast covering the Swan Coastal Plain. At the In-Situ Laboratory project site, the Guildford Clay formation, mainly consisting of clay with minor sand beds up to a thickness of 30 m, is predominant. The Superficial aquifer is recharged from direct rainfall above the aquifer as well as from the Yanget Mound located north west of the site. Groundwater salinity in the Superficial aquifer is variable at the project site but is widely used for stock and domestic purposes, except in areas of high salinity, associated with the Guildford Clay (Commander, 2013).

2.2. Leederville aquifer

The Cretaceous Leederville formation with a thickness varying from 108 m to 208 m, underlies the Superficial Aquifer in the project area. At the project site, the Leederville is mainly shale and contains very few aquifer horizons and is recharged from the overlying superficial aquifer in the area of the Yanget groundwater mound (Commander, 2013). Groundwater salinity is quite variable, both spatially and with depth. Due to a large thickness of clays and poorly developed sand beds in the Leederville, the aquifer is poorly developed in the vicinity of the project site. To date, the groundwater has been used for mining in the township of Cookernup (Commander, 2013).

2.3. Eneabba aquifer/aquitard system

The Early Jurassic Eneabba aquifer/aquitard system occurs directly

Fig. 6. Picarro setup for measuring atmospheric CO_2 concentrations 10 cm above the ground surface.

Table 2
Summary of the Li-COR data obtained during the project.

Chamber	Location	CO_2 flux (average ± 1σ)	
		Before injection from 16 Jan to 4 Feb ($g\ m^{-2}\ d^{-1}$)	After injection from 11 Feb to 21 Mar ($g\ m^{-2}\ d^{-1}$)
1	Next to the monitoring well	9.75 ± 3.35	5.72 ± 3.68
2	Between the monitoring and injection well	13.54 ± 3.41	4.58 ± 3.95
3	Next to the injection well	10.11 ± 4.58	10.56 ± 2.88
4	~30 m away from the injection well	7.56 ± 1.19	6.13 ± 1.10

Fig. 7. Soil gas sampling setup and method for collecting gas samples. Note the soil gas sampling interval is 2 m below ground level and surficial soil cracking.

under the Leederville Aquifer. In the project area, the salinity exceeds 20,000 mg/L and suggests the aquifer could be isolated by the faulting of the formation, with water not recharged by the meteoric water cycle (Commander, 2013). The Eneabba aquifer is not used for groundwater supply due to its depth and high salinity.

3. In-Situ Laboratory project site overview

For this project, 38 t of gaseous (or subcritical) CO_2 was injected into an approximately 7 m interval of a faulted reservoir at a depth of approximately 340 m (Fig. 1) over a period of approximately 6 days. In the direction of the subsurface faults, an observation well was drilled and completed with a fiber glass casing approximately 7 m laterally away to the depth of the injection interval. The injection well was equipped with a downhole pressure sensor and a fiber optic cable for distributed temperature and acoustic sensing. The observation well was equipped with electro-resistivity probes, seismic geophones and a fiber optic cable for distributed temperature sensing. As part of the characterization and monitoring program at the site, the focus was on understanding potential leakage pathways through the soil (via the faults, etc. in the subsurface) or along the casings of the wells (see Fig. 1).

4. Monitoring program

4.1. The surface gas monitoring program

The two primary aims of the surface gas monitoring program within this project are to demonstrate compliance with the project's environmental management plan and to identify and attribute any changes in the CO_2 concentration or soil-gas flux in the vicinity of the wells/wellpad before, during and after the injection activities. The surface gas monitoring component of the project looks for elevated CO_2 signals in the soil zone or at the ground surface in addition to evidence of small seeps at the ground surface. If anomalous reading are detected, the surface monitoring program strategy proceeds to an attribution phase to understand the underlying causes. This involves characterising the suspected leak through more intensive soil gas sampling, looking at gas ratios, gas composition and isotope analysis. The next step in the escalation pathway would be to estimate the quantity of CO_2 being leaked and this could be accomplished using a co-release of chemical tracers such as acetylene. This can be achieved through integrating soil flux analysis (Schroder et al., 2017) or atmospheric quantification techniques (Feitz et al., 2018a). Finally, if the CO_2 leak were considered substantial in size, an impact assessment would be conducted to measure the degree of environmental damage or decrease in the environmental asset utility (e.g. degraded groundwater quality). Similar to the methods used in our regional greenhouse gas emissions surveys, we

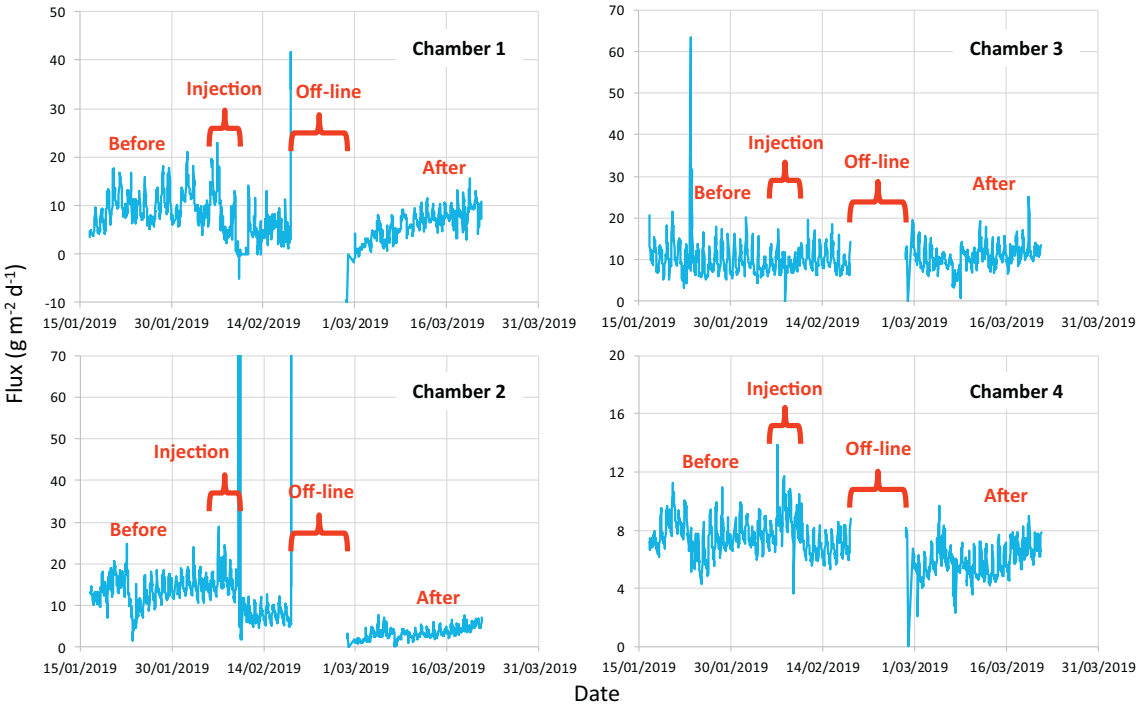

Fig. 8. CO_2 soil flux over time measured using the Li-COR instrument.

have combined both long-term fixed-site measurements with periodic mobile surveys for this project (Myers et al., 2019). In this way, we can maximize the efficiency of the surface gas monitoring program and reduce extraneous resources devoted to the surface monitoring component of the project.

4.2. Ground water sampling program

Similar to other demonstration sites, the primary goals of the groundwater monitoring program for this project are to be able to detect whether any changes in the physical and chemical conditions of the aquifers have resulted from the CO_2 storage activities, including the drilling, pressure changes and storage of CO_2 (Caritat et al., 2013). This involved monitoring groundwater levels and measuring groundwater quality before and after CO_2 injection near the site (Fig. 2). Groundwater sampling occurred in two shallow groundwater wells in the Perth Superficial Aquifer (i.e. In-Situ Lab groundwater well and stock bore) and two deeper wells in the Eneabba aquifer (Harvey-2 injection well and ISL-OB1). These wells are all located within a 1 km radius of the injection well, Harvey-2 (Fig. 3). The reasons for measuring groundwater levels in this kind of experiment is to make sure that: a) drilling activities at the observation well are not impacting the Perth Superficial aquifer, b) subsequent activities onsite associated with injection of CO_2 are also not impacting and c) confidence is provided to community and regulatory authorities that CO_2 activities have not impacted the Perth Superficial aquifer, which is an important aquifer supplying water for stock. Aquifer water chemistry was monitored as the injection of CO_2 underground into rock formations containing brines can push brine and CO_2 out of the original reservoir through possible leakage pathways into groundwater aquifers causing their contamination by heavy metals, NaCl and other major ions (Trautz et al., 2013; Wisotzky, 2011).

5. Methods

5.1. Surface gas monitoring program

Baseline monitoring commenced on 16 January 2019, prior to injection which started on the afternoon of 5 February 2019 and concluded on the 10 February 2019. Table 1 summarises the different monitoring methods and techniques included in the In-Situ Lab site gas monitoring survey. It provides details of the setup, measurement frequency and number of samples/data points collected before, during and after CO_2 injection. Fig. 3 is a map of the site that shows the location of the injection and monitoring wells as well as the grid points (used for the periodic soil-gas flux chamber measurements), the shallow groundwater well and five shallow soil-gas wells (at a depth of approximately 2 m). In the period prior to injection, data was collected on both the near-surface atmospheric CO_2 concentrations and soil-gas flux to establish the baseline variations. During injection, certain monitoring methods (i.e., Picarro CRDS) were not deployed due to interferences from likely elevated atmospheric CO_2 levels arising from various site activities (i.e., generators, heating during injection, CO_2 venting for the pumping systems, vehicle emissions). Post-injection monitoring comprised mainly of soil-gas flux measurements along with some periodic surveys using the Picarro CRDS.

The site has very distinct climatic seasons with the summer months being generally quite hot and dry with very occasional rainstorms and the winter months being generally cooler and having regular rainstorms. The map shows the arid landscape of the site during the summer as well as the location of a water tank and the extent of the crushed limestone well pad. Immediately outside of the well pad, there are crevasses (some of them as deep as 1.5 m and 20 cm wide, see pictures in Fig. 7 of typical ground just outside the area of the crushed limestone well pad) on the surface resulting from the drying of the clay soil layer during the dry summer months. Given the difficulty in obtaining soil-gas flux measurements on this type of surface (due to poor sealing of the flux chambers with the ground) during the summer months in which this project took place, it was decided to concentrate soil-gas flux measurements over the limestone pad for all surveys (Figs. 4 and 5). It was considered that the near-surface mobile atmospheric gas surveys (Fig. 6) would be more effective for leak detection over the cracked soil terrain.

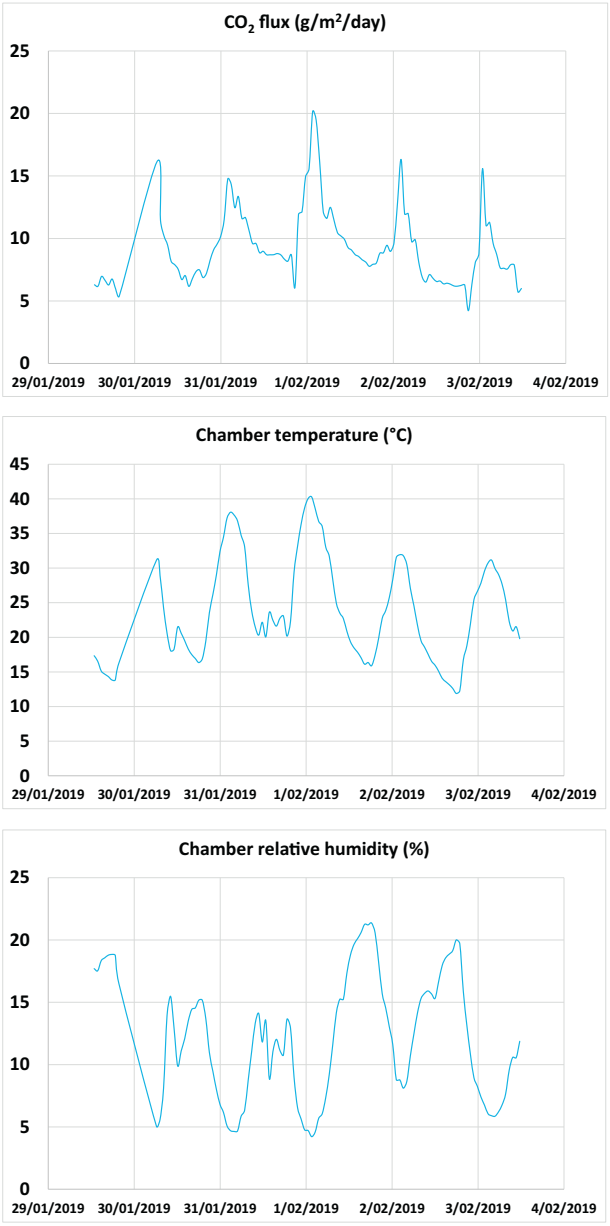

Fig. 9. CO_2 soil-gas flux, RH and temperature as measured at chamber 3 over a period of approximately 5 days.

5.2. Groundwater monitoring program

5.2.1. Groundwater levels

To monitor the variations in groundwater level as well as electrical conductivity, both an In-Situ Aqua Troll 200 level logger and a Solinst barometric logger for atmospheric pressure correction, were installed in the In-Situ Laboratory groundwater well completed in the Perth Superficial aquifer (see Figs. 1 and 2). The loggers were programmed to continuously log readings at an interval of 1 min and data were downloaded from loggers at regular intervals. During each groundwater sampling trip, water levels were measured manually using a 100 m Solinst Interface Meter (Model 122) and recorded, providing an independent check of the logger data. The loggers also measure the temperature of the standing water column at the depth of the logger, which can be extrapolated downward to the aquifer using a known regional temperature gradient. Recorded data are compensated for variations in the barometric pressure/water density and corrected to the Australian Height Datum (AHD).

5.2.2. Water quality sampling

Three groundwater sampling campaigns took place before CO_2 injection started at Harvey 2 (between November 2018 and January 2019), three during the injection period and five after injection finished (February–March 2019). The spatial location of the sampled bores (In-situ Laboratory groundwater well ISL-GW, In-situ Laboratory observation well ISL-OB1, stock bore and Harvey 2 injection well) is shown in Fig. 2. At each bore, the pumped water was monitored for pH, Eh, electrical conductivity (EC), dissolved O_2 (DO) and temperature (T) using Eureka Manta 2 Multiparameter water quality meters until stable values were recorded. The groundwater well was purged for a minimum of three to five well volumes. During sampling, steady state conditions were maintained, field parameters were monitored regularly, and groundwater sampling only occurred when field parameters were stabilized within a range outlined in the Australian Standards for Water Quality Sampling.

The following analyses were performed at each sampling location: field parameters, anion composition, cations (including trace) composition, alkalinity, dissolved CO_2 concentration, total inorganic carbon (TIC)/total carbon (TC)/total organic carbon (TOC) composition and the carbon isotopic composition of the dissolved inorganic carbon.

The suite of samples taken at each well was as follows:

- Raw water (PE container filled to top) for alkalinity/major anions and cations/TIC/TC/TOC/Isotopic analysis of TIC
- Filtered (0.45 μm) water, acidified to pH < 2 (PE container filled to top) for trace cation analysis
- Raw water (100 mL glass serum bottle filled to top with flowing water while immersed in the water and septum-sealed) for dissolved carbon dioxide
- Raw water (2 × headspace vials filled to the top preserved to pH < 2) for BTEX (benzene, toluene, ethylbenzenes and xylenes) and C6-C10 petroleum hydrocarbons.
- Raw water (500 mL brown bottle) filled to the top for total recoverable hydrocarbons (TRH) and polycyclic aromatic hydrocarbons (PAHs).

After collection, samples were kept cool (< 6 °C) and transported to the CSIRO Perth NGL Laboratory for analysis. Samples which required analysis by an external laboratory were transported as per external laboratory sampling and handling procedures. The sampling procedures used were based upon Australian/New Zealand water quality sampling guidelines (AS/NZ 5667.1) and relevant American Public Health Association (APHA) guidelines.

5.2.3. Analysis of water samples

Major anions in the groundwater samples were analysed using the US EPA Method 9056A (Ion Chromatography). The instrument used was a Thermo Scientific IC-4000 system fitted with a Dionex IonPac AG-18-4 m 150 mm column using potassium hydroxide solution as the eluent. Alkalinity was determined using US EPA Method 310.2 on a Methrohm Auto-titrator. Major cations in water were analysed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrophotometry) using the US EPA Method 200.7 on an Agilent 725 radial instrument. Trace elements in water were analysed by ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) using the US EPA Method 310.2 on an Agilent 7700 instrument.

The abundances of the dissolved gases in the water samples were determined by headspace analysis using the US EPA RSK-175 method. A 15 mL headspace was created in the serum sample bottles by simultaneously injecting 15 mL ultra-high purity helium through the septa with a second empty syringe withdrawing the same amount of water. The sample was subsequently vigorously shaken for about 3 min for the dissolved gases to accumulate in the headspace. Initially the first sample of the dissolved gases was used to determine the carbon isotopic value ($\delta^{13}C$) of the dissolved CO_2 from the water samples (see below).

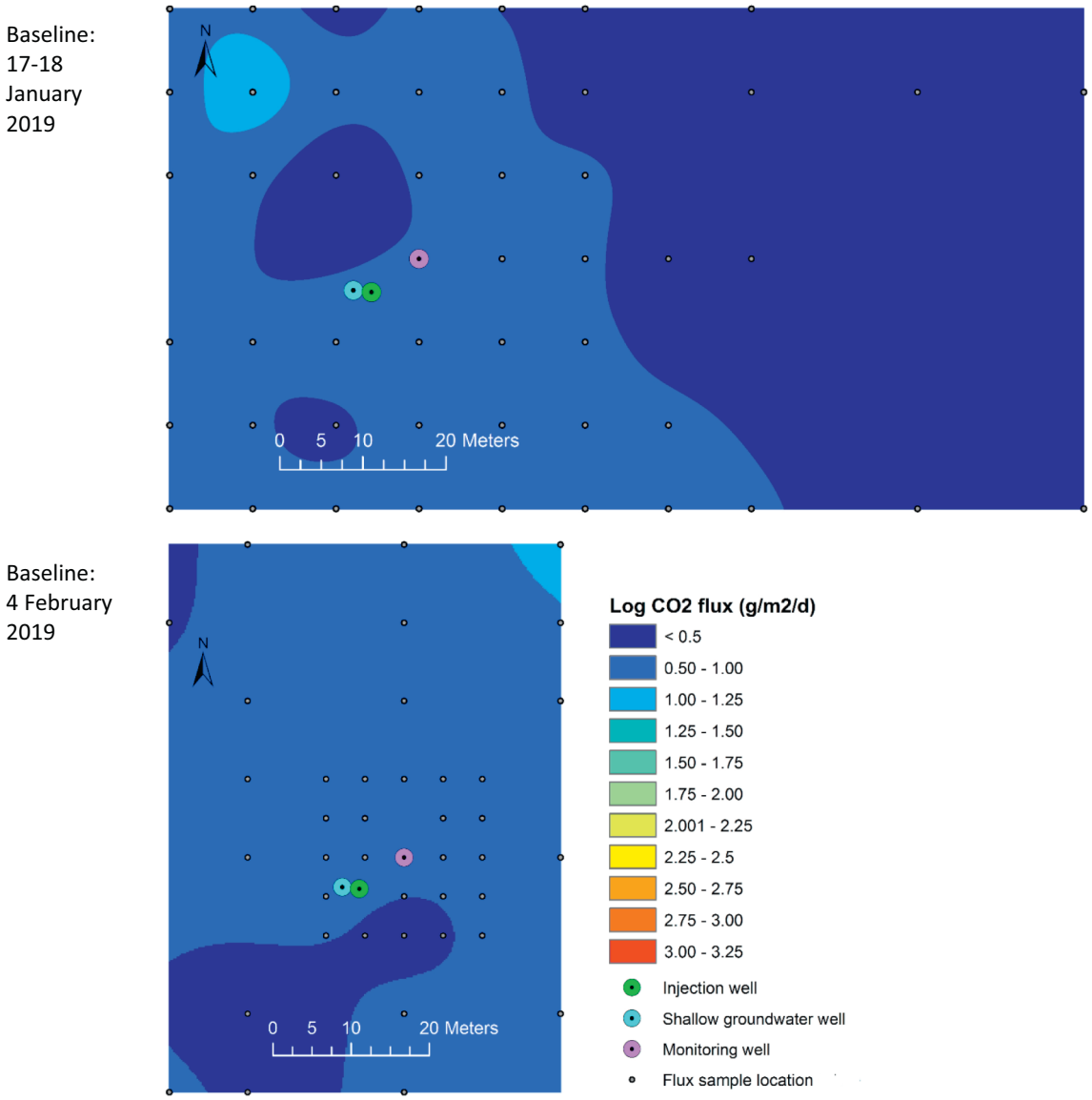

Fig. 10. CO_2 soil flux maps of the baseline surveys taken 3 weeks (17–18 January) and immediately prior (4 February) the CO_2 injection experiment.

After this approximately 5 mL of the headspace gas was injected on a ThermoFisher Refinery Gas Analyser gas chromatography system through a loop injector allowing quantification of the carbon dioxide present. These gas concentrations were subsequently converted into the dissolved gas concentration (mg/L) using Henry's Law equations and the Bunsen coefficient of the specific gas analysed at a specific temperature and salinity.

The $^{13}C/^{12}C$ ratios in CO_2 (expressed as $\delta^{13}C$-CO_2‰ vs. Vienna Pee Dee Belemnite (VPDB)) from dissolved gas samples and soil gases were determined with a Thermo Finnigan MAT 253 isotopic ratio mass spectrometer with a continuous flow injection from a Trace GC ultra-fitted with an Agilent Poraplot Q column connected to a Thermo Finnigan GC-Isolink.

The carbon isotopic value ($\delta^{13}C$) of dissolved inorganic carbon from the water samples was determined from 2 mL water sub-samples which had been filtered through a 0.45 μm syringe filter. Exetainer vials (12 mL) were dosed with 100 μL of 42% phosphoric acid, capped and flushed with helium to remove any entrained CO_2 from air before the raw water samples were injected into them. The evolved gas from any inorganic carbon present was subsequently sampled by the gas bench and measured on a MAT253 isotope ratio mass spectrometer.

TIC/TC/TOC in water samples were analyses using methods based on EPA method 415.1. where the measuring principle is the oxidation of bound carbon into CO_2. The liquid sample was directly injected into the combustion reactor at 900 °C in an air carrier gas stream. The gas was dried, flow stabilized and measured by means of a non-dispersive infrared (NDIR) detector. A connected computer calculates the total carbon concentration (TC) from the measured CO_2 signal and the sample weight/volume. Inorganic carbon (TIC) is measured automatically by acidifying the sample in a sparger and the released CO_2 is quantified. Total organic carbon (TOC) content is calculated from the difference of the TC and the TIC (i.e. TOC = TC-TIC). Organic analyses were subcontracted to a third-party laboratory who analysed the samples using methods based on the following: USEPA methods 8260b, 3510 and 8270.

6. Results and discussion

6.1. Fixed-site soil-gas flux monitoring

Continuous soil gas flux measurements were made at four different locations using a Li-COR instrument (Fig. 2). The CO_2 soil flux was

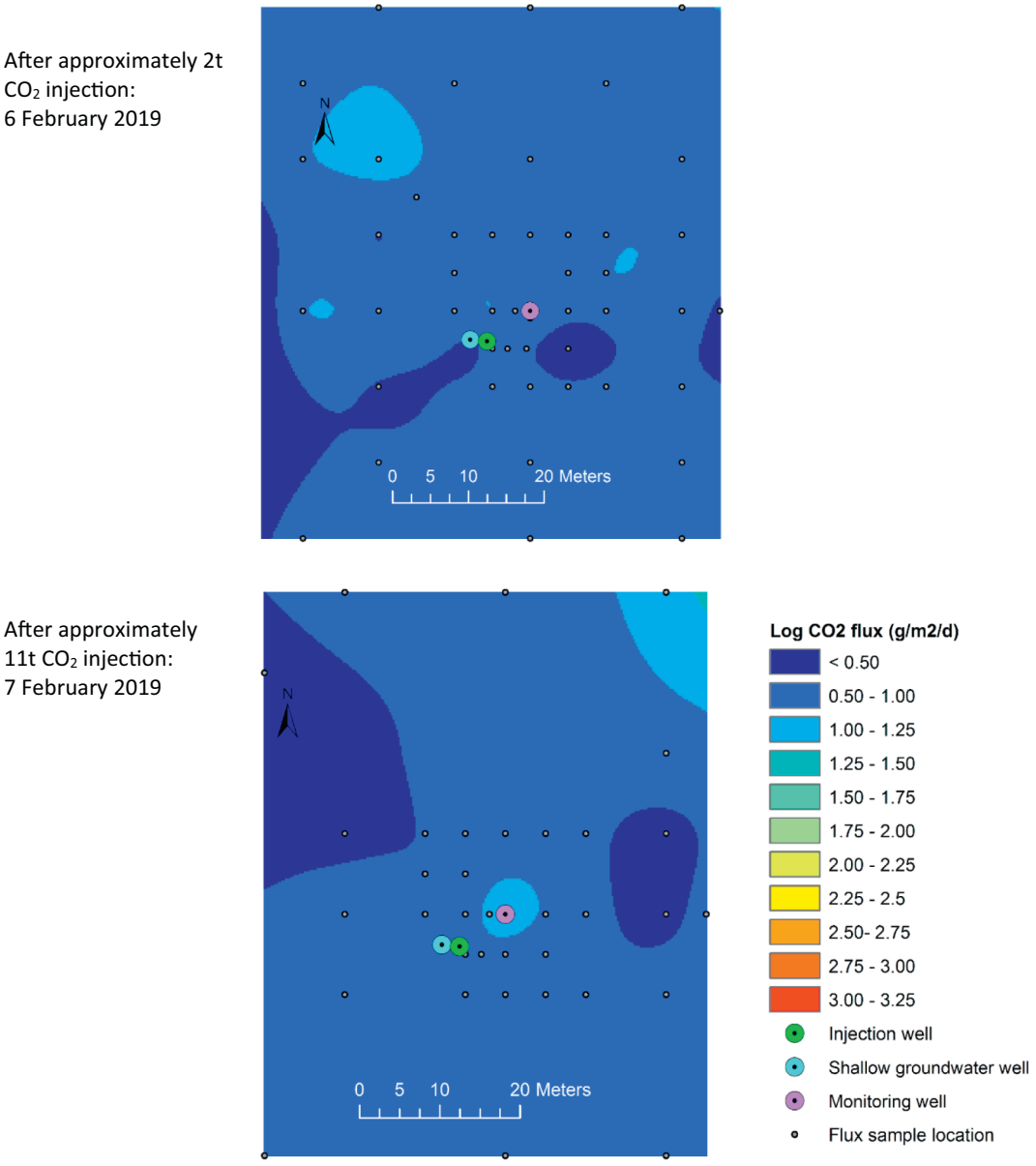

Fig. 11. CO_2 soil flux maps during and after the completion of the CO_2 injection experiment.

measured near the monitoring well (chamber 1), between the monitoring and injection wells (chamber 2), near the injection well (chamber 3) and far away from the wells (chamber 4). The CO_2 soil flux that was measured from 16 January 2019 to 21 March 2019 are shown in Fig. 8. The fluxes for chambers 1, 2, 3 and 4 prior to injection generally varied between 3.43 and 21.02 g/m^2/d, 1.53–24.66 g/m^2/d, 3.19–31.67 g/m^2/d, and 4.28–11.22 g/m^2/d, respectively. These values are consistent with typical CO_2 soil fluxes that have been published in the literature (Madsen et al., 2009). Variations in the soil-gas flux can often be attributed largely to diurnal fluctuations (Rayment and Jarvis, 2000; Richards et al., 2012). Fig. 9 shows an example of this diurnal fluctuation in the CO_2 soil-gas flux at chamber 3 over a period of several days. These changes are largely attributed to diurnal changes in the environment; for example, relative humidity and chamber temperature also have distinct diurnal fluctuations. The soil-gas flux values are generally lower at night/early morning and higher during the day.

Some high flux values (45–63 g/m^2/d) were observed in chamber 3 for a very short period (< 1 h) on the 23 January 2019 and is most likely due to various organic-based materials (leaves, etc.) that had accumulated in the soil collar with time. During the injection period, elevated flux levels (40 to 549 g/m^2/d) were temporarily observed (over several hours) on the 10 February 2019 in chamber 2 (not shown on the chart in Fig. 8 due to axis scale). This is consistent with the event during the CO_2 injection that occurred following the subsurface casing breach in the monitoring well (on the evening of February 9th, the casing in the observation well failed due to over-pressurisation of the reservoir causing geyser-like activity to occur which emitted reservoir brine and CO_2). Discharge for each geyser-like eruption was estimated to be approximately 2750 L of formation water and 125 kg CO_2, based on wellbore volume and CO_2 solubility in water. In comparison, the Andernach Geyser in Germany with a well at similar depth and comparable eruption cyclicity is estimated to discharge 8000 l formation water and 350 kg CO_2 with each eruption (Wisotzky, 2011).

These high CO_2 flux values are largely attributed to CO_2 originating from the well head during the breach events and not soil-gas. Following this breach, injection of CO_2 was immediately suspended onsite. The flux in chamber 2 returned to baseline conditions immediately after injection (i.e., varied between 5 and 12 g/m^2/d). As for chambers 1, 3 and 4 the CO_2 soil flux during injection were almost identical and did not vary significantly when compared to the fluxes prior to injection.

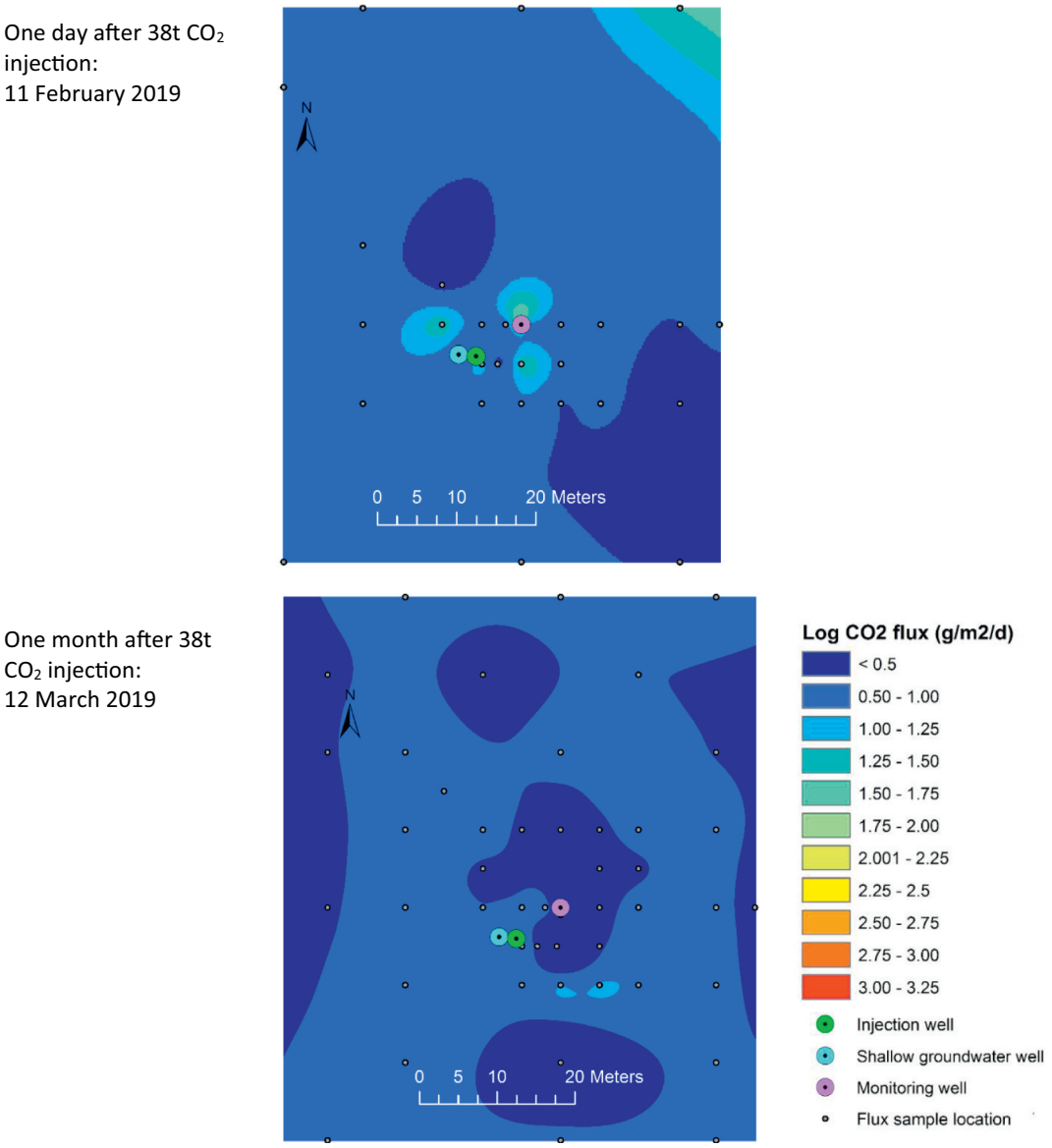

Fig. 11. (*continued*)

However, for chamber 1 (located next to the monitoring well) the data is sparse between 9 and 11 February given that it was removed from its location due to the flooding/breach event (caused by well breach mentioned above). Subsequently, the soil around the monitoring well was saturated with water and reliable flux readings from chamber 1 were difficult to obtain for this period. It is important to note that from the period between 19 and 26 February 2019 no flux measurements were made onsite due to instrument maintenance/repairs along with various well-remediation activities that required access to the monitoring/injection wells.

Table 2 summarises the CO_2 soil flux variations before and after injection for the four different chambers. Prior to injection, there does not appear to be any significant variation in the CO_2 soil flux when comparing the four different locations. However, the daily soil flux variations in chamber 4 (furthest from the injection well) seem to be slightly narrower compared to the other chambers (I, 2, 3). The CO_2 soil fluxes one month after injection were generally similar to that observed prior to injection. If anything, the soil fluxes particularly for chambers 1 and 2 appear slightly suppressed after the CO_2 injection; this could be attributed to the additional water from the well breach in the surrounding ground (Fig. 7, retained in the clay making up the soil under crushed limestone).

6.2. Soil-gas flux at gridded locations

Portable CO_2 soil flux surveys were undertaken at gridded locations onsite (Fig. 2 for locations) with a West Systems fluxmeter to obtain surface flux baselines prior to the CO_2 injection and monitor during and after the injection period. This methodology is similar to the work previously reported at the Ginninderra release site (Feitz et al., 2014a). The resulting interpolated CO_2 soil flux maps are given in Figs. 10 and 11. The baseline survey undertaken over the 17–18 January had a greater coverage than on 4 February and includes flux estimates taken over the very dry cracked soil to the east of the limestone pad (Fig. 7 for example of this). These fluxes were very low (< 0.2 log CO_2 flux ($g/m^2/d$)) compared to the flux observed over the limestone pad. The limestone pad CO_2 fluxes generally ranged from 0.5 to 1.0 log CO_2 flux ($g/m^2/d$) and were consistent between the two baseline surveys.

There was no evidence of surface CO_2 leakage after 2 t or 11 t of injection (Fig. 11). Although the data is sparse to the north of the injection well for the survey on 11 February (1 day after the completion of the 38 t injection and the well leakage event), there is evidence of

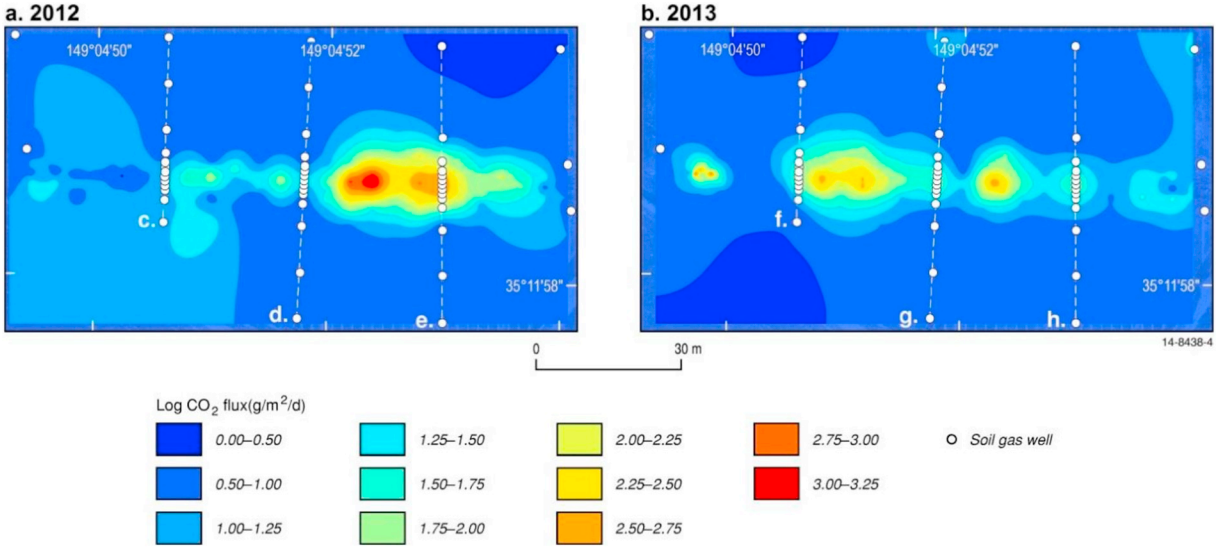

Fig. 12. Ginninderra CO_2 controlled release experiment soil flux maps (2012 and 2013) for comparison using the same scale as the In-situ Lab experiment (Feitz et al., 2014b). The total leakage rate during the Ginninderra controlled release experiments was 100 kg/d.

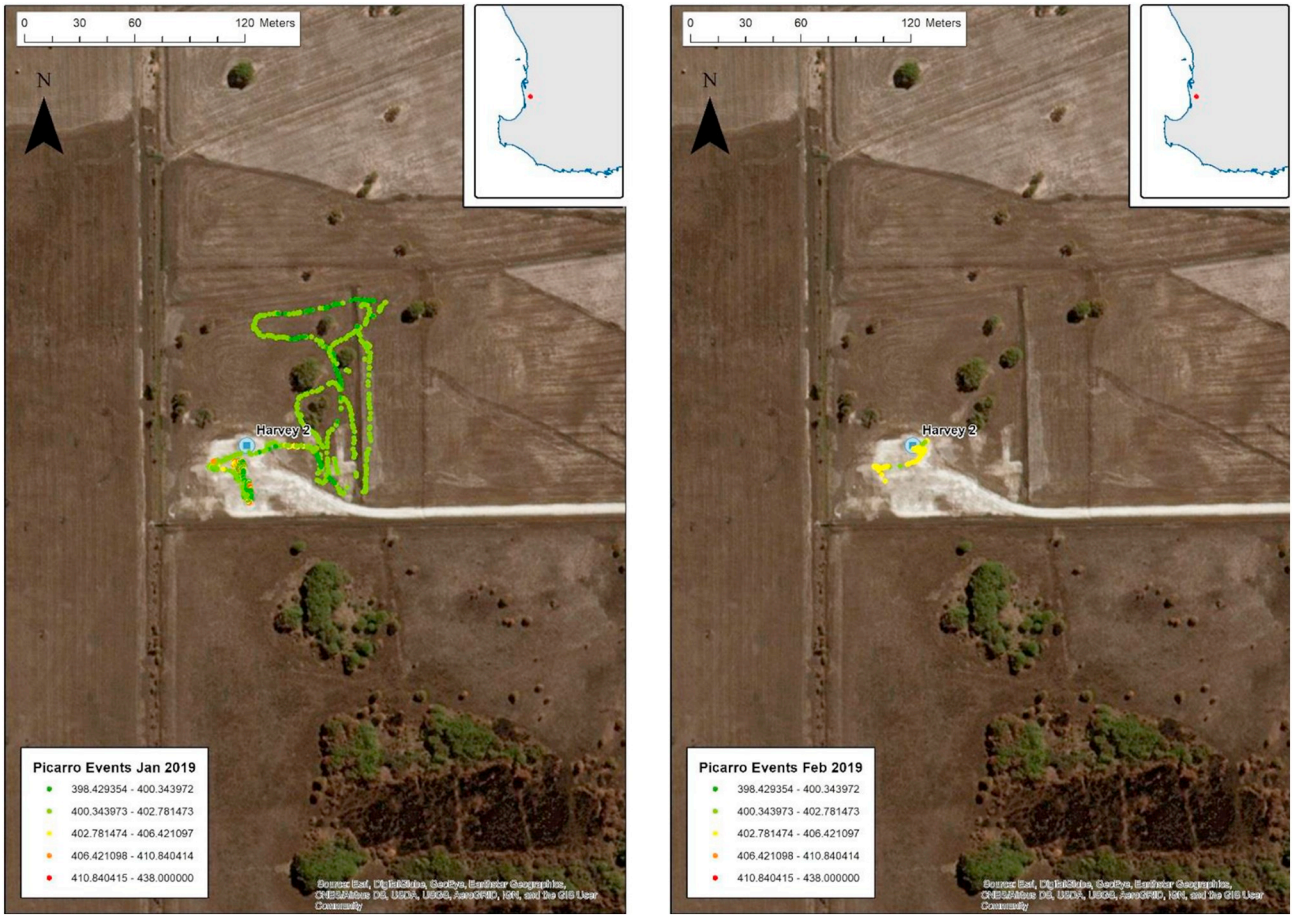

Fig. 13. CO_2 concentration measured over the Harvey 2 site using the mobile monitoring system.

elevated CO_2 flux values in the vicinity of the monitoring, injection and groundwater wells. Adjacent to the monitoring well, the maximum flux observed was 70 g/m^2/d. This is approximately 10 times above the average background CO_2 flux value across the limestone pad. As a comparison (Fig. 12), 70 g/m^2/d (or 1.85 log CO_2 (g/m^2/d)) would be considered a weak leakage signal at the Ginninderra controlled release experiment (Feitz et al., 2014b). The background soil flux levels at the Ginninderra experiment were similar to that observed for this project. The localised elevated levels were most likely due to flooding of supersaturated CO_2 groundwater around the well sites during the well leakage event at the In-Situ lab site. Elevated fluxes were also observed in the NE corner of the limestone pad on 11 February. This is located on the edge of the pad and may be influenced by residual CO_2 that could have accumulated in the soil cracks, particularly, due to venting during

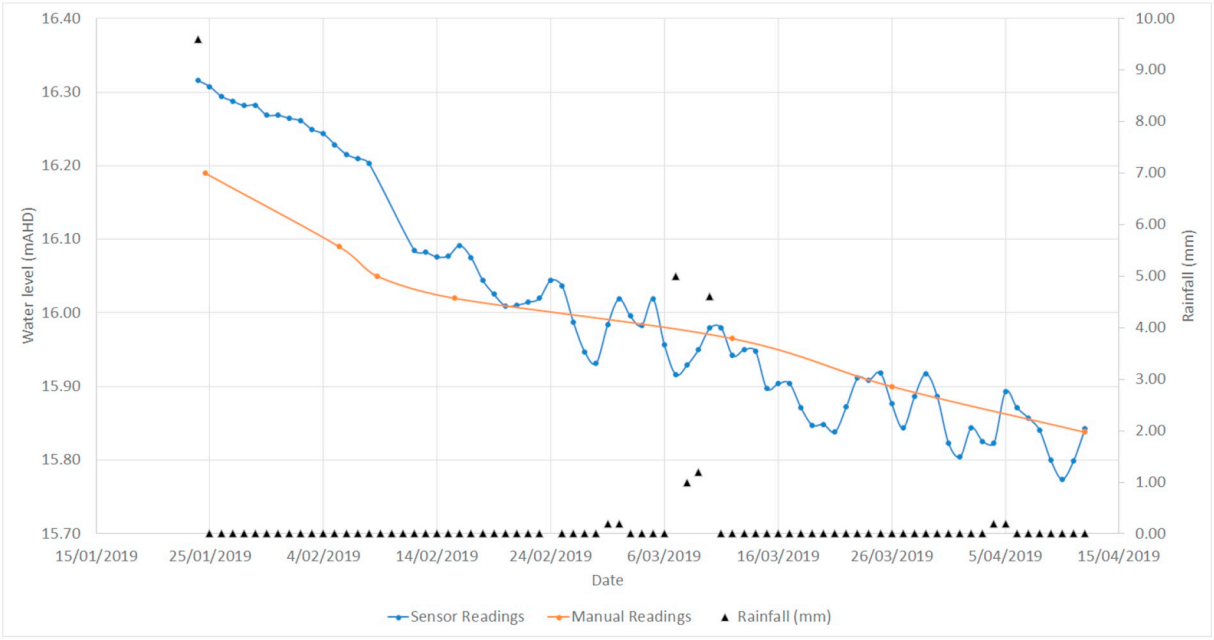

Fig. 14. Groundwater level data for the In-situ Laboratory groundwater well.

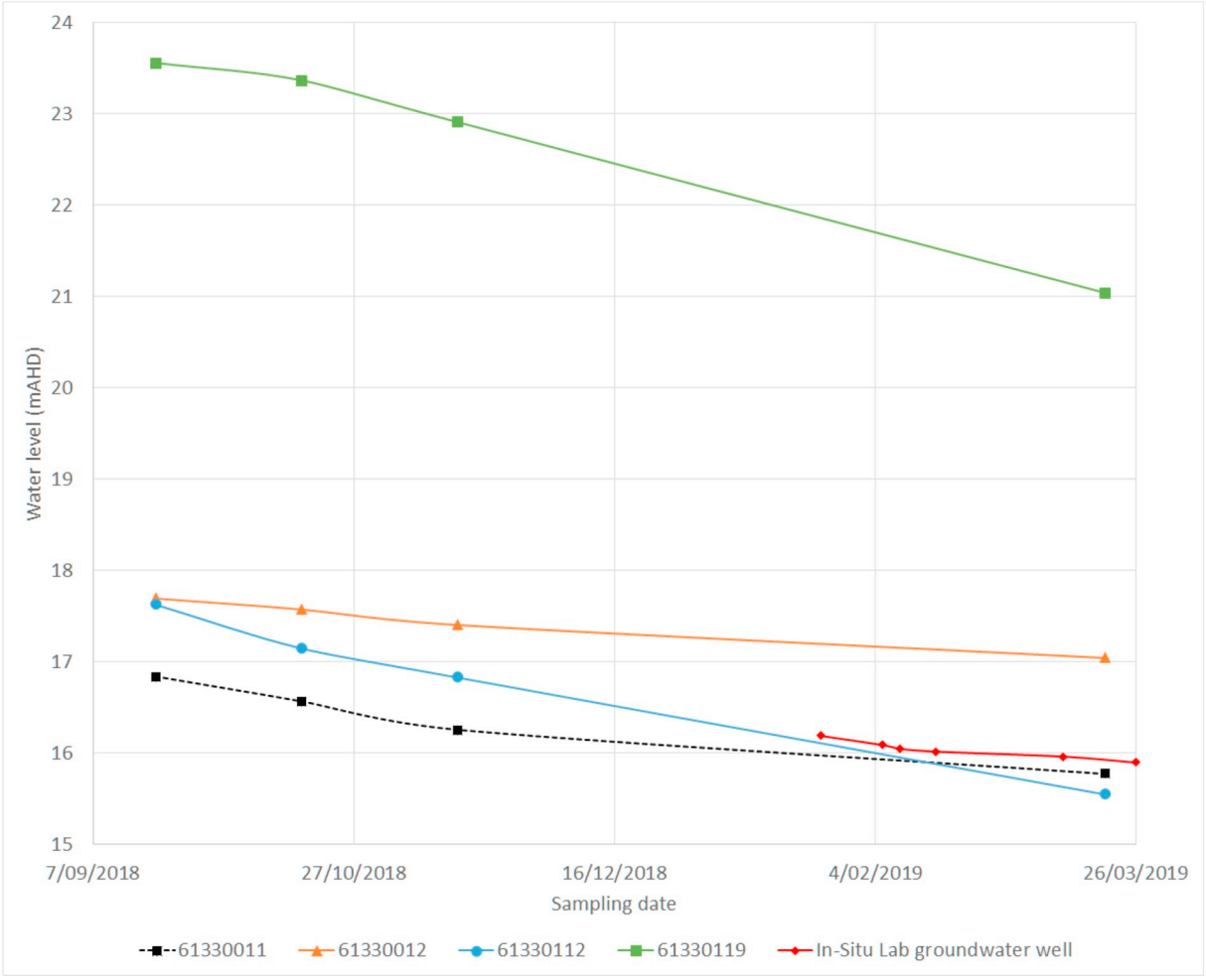

Fig. 15. Time series hydrographs for Perth Superficial aquifer wells. Source: WIR database.

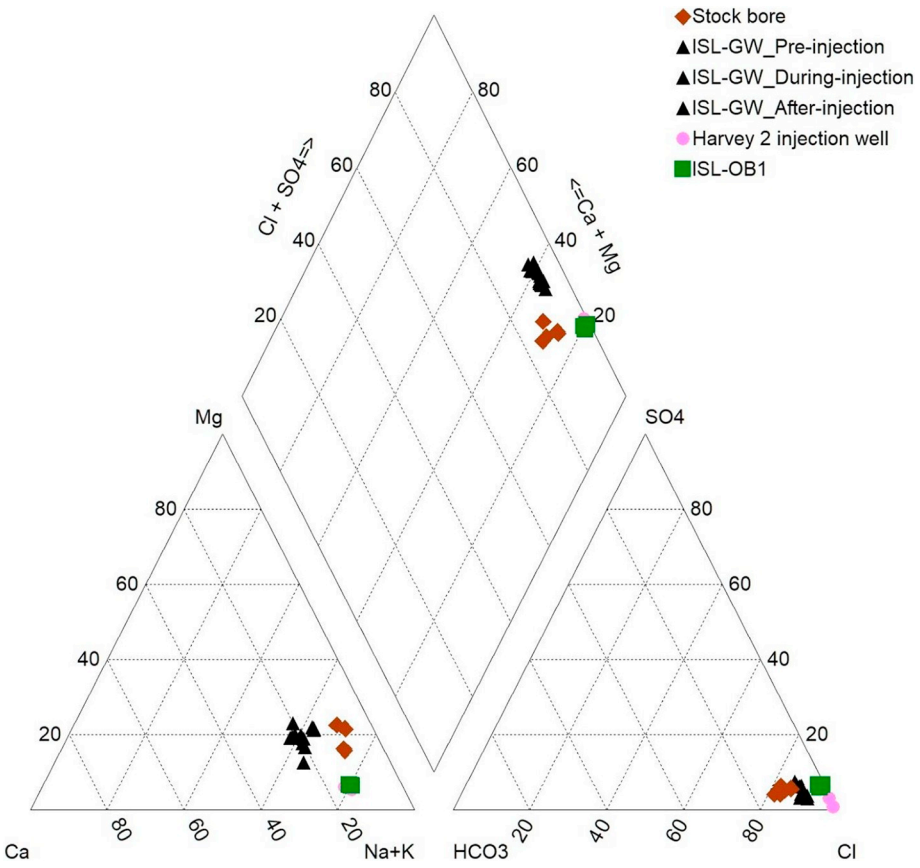

Fig. 16. Piper plot of the In-situ Laboratory project groundwater monitoring samples.

the CO_2 injection phase (to prime the injection system with liquid CO_2) or after approximately 1 t of CO_2 was released during the monitoring well leakage event. Survey results one month after the injection experiment (12 March) and 2 weeks after the remediation of the well indicate a return to baseline soil flux conditions (Fig. 11).

6.3. Near-surface atmospheric concentration

Surveys were also undertaken with a mobile CRDS system with GPS tracking to investigate the variations in the atmospheric CO_2 concentration. This is similar to the strategy used at the release experiment at Ginninderra (Feitz et al., 2014a). The measurement of CO_2 concentrations was determined by sampling at a constant height (10 cm) above the soil surface and was performed when the wind speeds were relatively low. Surveys prior to injection (from 16 to 30 Jan 2019) were performed over the entire site both on the limestone pad and adjacent to the limestone pad in the grass/clay area. However, the mobile CRDS surveys post injection (12 Feb 2019, 27 Feb 2019) were focussed primarily around the wells on the limestone pad. The aim of the measurements were to rapidly assess the CO_2 concentration at high resolution and to identify deviations in the CO_2 concentration relative to backgrounds levels. Fig. 13 shows the CO_2 concentration profile around the Harvey 2 site before and after CO_2 injection. Prior to injection (30 January 2019), the CO_2 concentration in the air above the soil surface varied mainly betw0een 398 to 406 ppmv. There were some high values and CO_2 spikes above 406 ppmv which were located south of the wells and this is probably attributed to various activities occurring on site (i.e., vehicles, diesel generators on). Measurements two weeks following injection (27 February 2019) revealed CO_2 concentration variations of between 400 and 406 ppmv. No significant leaks were detected relative to the background in the dataset post injection and the values around the wells were generally commensurate with the readings obtained prior to injection. The average CO_2 concentration prior to injection was 402.7 ± 3.9 ppmv and this is in agreement with the global average atmospheric carbon dioxide levels. The average CO_2 concentration post injection (27 February 2019) was 403.1 ± 0.3 ppmv.

6.4. Soil-gas wells

Five wells installed mainly on the north part of the Harvey 2 site were used for gas sampling of the soil vadose zone and the procedure used is described elsewhere (Schroder et al., 2017). Fig. 13 shows the location of the wells (i.e., soil gas 1, soil gas 2, soil gas 3, soil gas 4 and soil gas 5) and gas samples were collected at various stages. The location of the sampling sites was selected to provide background soil gas samples for the experiment, not for detection of leakage. Any suspected surface leakage detected using the Picarro or soil flux systems would escalate the surface monitoring program to an attribution phase, where intensive soil gas sampling at the suspected leakage site (including installation of new wells) would have been employed. The five wells are designed to provide background measurements for any potential leak attribution analysis. Sampling was undertaken on 19th and 30th of January 2019 (before injection), 5th and 8th of February 2019 (during injection) and on 21st February 2019 (after CO_2 injection). Samples were submitted for carbon isotope and gas composition analysis. Carbon isotope analysis (^{13}C) was performed by direct injection into a Thermo Scientific Mat253 gas chromatography isotope ratio mass spectrometry (CG-IRMS) system and Table 3 displays the results of this study.

The ^{13}C ranged between −22.1 to −31.9‰ VPDB for all gas samples that were collected. To date there does not appear to be any significant variations in the ^{13}C of the soil gas before, during and after CO_2 injection. Table 3 also shows the results of the injected CO_2 that was

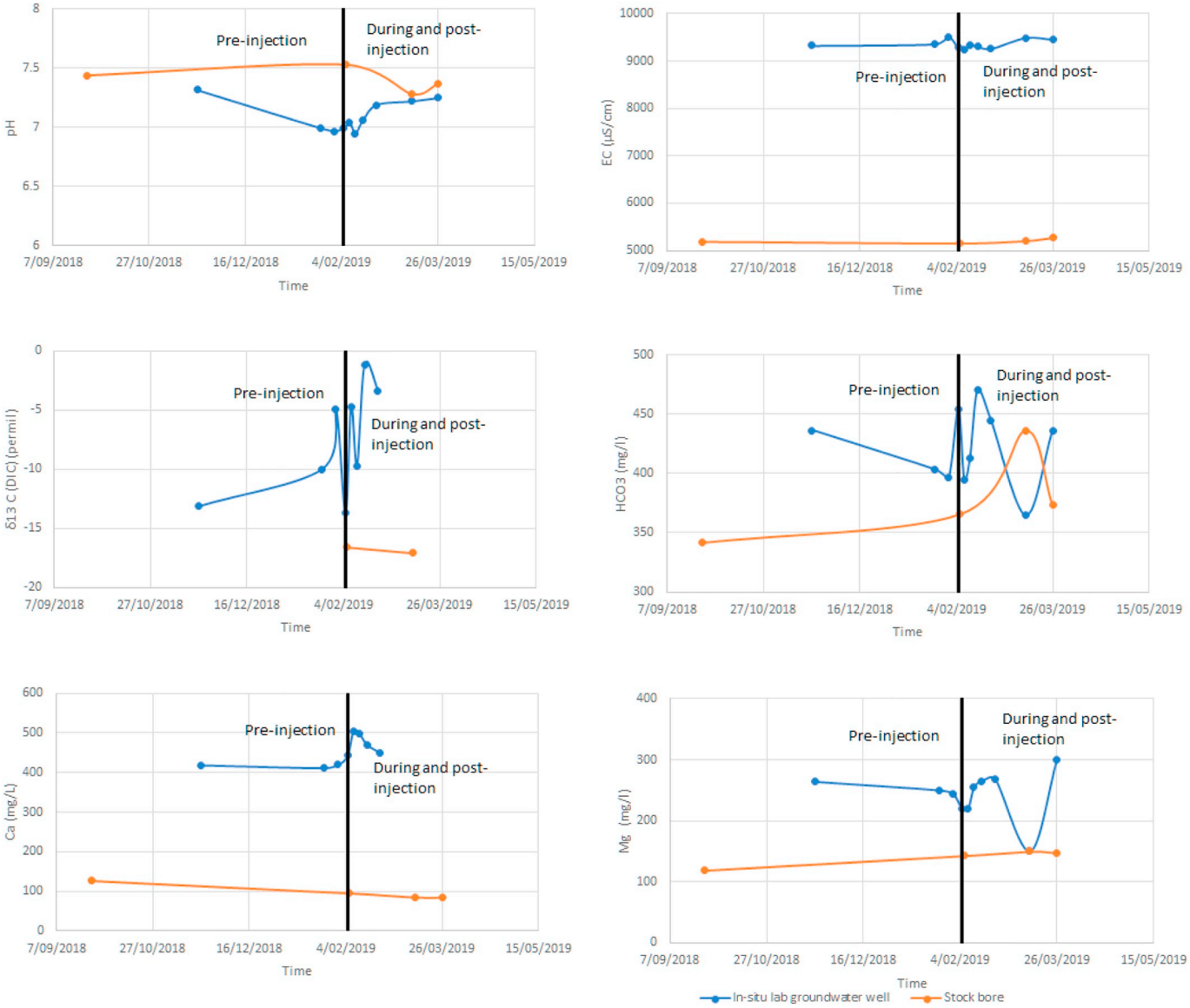

Fig. 17. Time series plot for selected water quality parameters for In-Situ Laboratory groundwater well (blue colour line) and stock bore (orange colour line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

used in this project (Harvey inlet 1 and 2) which is of a petroleum origin. Baseline (19 January 2019) and injected CO_2 samples were independently tested at Geoscience Australia. The injected CO_2 is significantly more depleted in ^{13}C (−42‰ VPDB) compared to the biological respired carbon dioxide observed in the soils before injection occurred. If any injected CO_2 were to leak into the soil vadose zone one would expect that the soil gas ^{13}C isotopic composition would be more depleted, however, the soil gas isotopic values after injection show a limited variability and the average ^{13}C value of the CO_2 (−26.6‰ VPDB) is nearly identical to what was observed before injection. It is important to note that some of the wells (soil gas 4) often produced water during sampling and it was difficult to collect suitable gas samples. Irrespective, the observed soil gas isotopic composition is consistent with biological respired carbon dioxide.

6.5. Groundwater level trends

A total of 137,339 groundwater level measurements were recorded using an In-Situ Aqua Troll 200 level logger during January–March 2019 and this data was converted to standard meters above Australian Height Datum (mAHD). Fig. 14 shows the daily mean groundwater levels measured between 25th January and 12th April 2019. Rainfall data for the Harvey meteorological station was obtained from the WA Department of Primary Industries and Regional Development's weather website and are shown in Fig. 14. On 25th January and 26th February 2019, due to malfunction of pressure sensor, the level logger recorded erroneous readings. On 26th February 2019, the existing In-Situ Aqua Troll 200 level logger was replaced with another calibrated In-Situ Aqua Troll 200 level logger. A general decrease in groundwater level is observed between 26th February and 12th April 2019, which is confirmed by manual readings recorded using a 100 m Solinst Interface meter (Fig. 14).

Fig. 15 shows water level trends for four Perth Superficial aquifer wells (as shown in Fig. 2) monitored by the Western Australia Department of Water and Environmental Regulation and located within 10 km radius of the In-Situ Lab groundwater well. During September 2018–March 2019, a decrease in groundwater level was observed in the Department of Water and Environmental Regulation's groundwater wells, which is consistent with the trend observed in the In-Situ Lab groundwater well. In the In-Situ Laboratory project site, groundwater

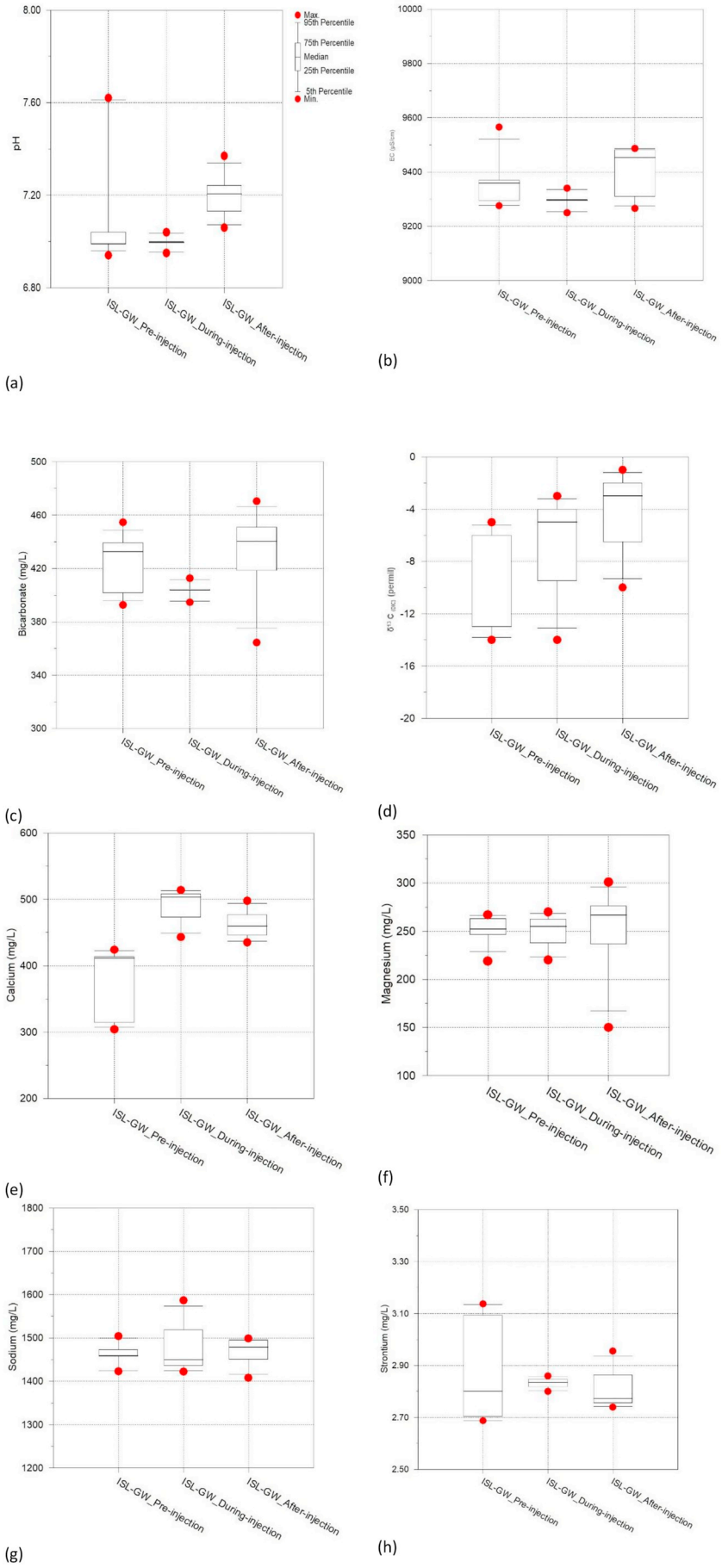

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Fig. 18. Boxplot pairs from the Perth Superficial aquifer comparing the pre-, during- and post-injection data for (a) pH, (b) EC, (c) bicarbonate, (d) $\delta^{13}C_{(DIC)}$, and concentrations of (e) calcium, (f) magnesium, (g) sodium and (h) strontium. ISL-GW = In-situ Laboratory groundwater well.

Table 3
The carbon isotope (^{13}C) data obtained on the gas samples which were collected from the soil gas wells. ND = not determined and this is because significant volumes of gas could not be obtained for analysis.

Sample	‰ $\delta^{13}C$ (VPDB)				
	Before injection[a] (19 Jan 2019)	Before injection (30 Jan 2019)	During injection (5 Feb 2019)	During injection (8 Feb 2019)	After injection (21 Feb 2019)
Soil Gas 1	−31.3	−26.8	ND	ND	−25.9
Soil Gas 2	−22.1[b]	−27.8	−27.2	−27.6	−23.5
Soil Gas 3	−31.9	−26.0	−27.9	−26.4	−28.0
Soil Gas 4	−28.5	ND	ND	ND	ND
Soil Gas 5	−26.4	−26.7	−25.3	−27.0	−27.7
Harvey inlet 1		−42.0 (−41.6)[a]			
Harvey inlet 2		−42.4 (−41.6)[a]			

[a] $\delta^{13}C$ analysis conducted at Geoscience Australia.
[b] CO_2 concentration low and possibly contaminated with air, affecting the $\delta^{13}C$ result.

flow is in a northwest direction i.e. from the Darling Scarp towards the Yanget Mound and is consistent with the flow patterns reported for the Perth Superficial aquifer (Blomestein, 2016; Commander, 2013).

Based on groundwater level data obtained during January–March 2019, observed groundwater level fluctuations in the In-Situ Lab groundwater well can be attributed to the natural variations occurring in other parts of the Perth Superficial aquifer. No impacts from injection of CO_2 into deeper aquifers (Eneabba) on water levels in the Perth Superficial aquifer were observed. This is not unexpected as the Perth Superficial aquifer is separated from Eneabba by thick layers of shale/sandstones and other aquitards and aquifers (see Fig. 1).

6.6. Groundwater composition measurements

Nearly 43 quality-controlled groundwater samples were collected during January–March 2019 and are summarised in Table 4, grouped relative to injection. The Perth Superficial aquifer groundwater is brackish (electrical conductivity = 9276–9565 µS/cm), cool (T = 18.9–26.4 °C) and near-neutral pH (pH = 6.94–7.62). The Eneabba aquifer groundwater is saline (electrical conductivity = 48,850–55,580 µS/cm), cool (T = 21.48–31.99 °C) and near-neutral pH (pH = 6.48–7.06).

A Piper diagram (Fig. 16) shows that the Perth Superficial groundwater (In-Situ Laboratory groundwater well and Stock bore) is dominantly of the Na—Mg—Cl (7 samples), Na—Cl (6 samples), Na—Ca—Cl (6 sample); Na—Ca—Mg—Cl (two sample) and Na—Mg—Ca—Cl (one sample) types. The Eneabba Aquifer groundwater is quite different from the Perth Superficial groundwater and both bore represents a similar water type: Na—Cl (six samples) (Fig. 16).

6.7. Comparing pre- and post-injection water composition

Fig. 17 illustrates time-series for selected water parameters of relevance to CO_2 storage: pH, EC, $\delta^{13}C_{(DIC)}$, HCO_3^-, Ca^{2+} and Mg^{2+} concentrations, for wells targeting Perth Superficial aquifer. Fig. 18 illustrates differences between water quality characteristics of the pre, during and post CO_2 injection. Boxplots clearly indicate that changes between the pre-, during- and post-injection subsets are not statistically significant. Leaked CO_2 gas from depth into the near surface aquifers, if it were to occur, would result in a reduction of pH (or increased alkalinity if the reduced pH caused a reaction), increased concentrations of dissolved HCO_3^-, Ca^{2+}, Mg^{2+}, Fe^{3+} and changed in EC and, $\delta^{13}C_{(DIC)}$ (Caritat et al., 2013). However, no such trend is observed for Perth Superficial groundwater sampled during February–March 2019.

In Table 4 the last column on the right shows the difference in median values for the parameters relevant to CO_2 storage after injection compared to before. A comparison of the values in this column to the median absolute deviation (MAD) values with either the pre, during and post-injection data shows that the changes are in almost all cases less than MAD, and, therefore, within the natural variation and/or sampling and analytical error of the data. However, potentially significant differences in median and MAD values were observed for Ca^{2+}, K^+ and $\delta^{13}C_{(DIC)}$.

The increase in Ca values between pre- and post-injection, could be due to dissolution of calcite from limestone well pad overlying the clay formation, from either rainfall or water from the flooding of the well pad due to the well casing breach (Fig. 14). The increase in K^+ could be contributed to spillage of drilling chemicals used during construction of ISL-OB1 and In-situ laboratory groundwater well and subsequent leaching of these chemicals from well pad/clay formation into the aquifer. Elevated level of $\delta^{13}C$ could be either due to seepage of

Table 4
Statistical summary of analyses of Perth Superficial groundwater.

Parameter	Unit	Pre-injection		During and post injection		Difference in median values post-injection compared to pre-injection
		Median	MAD	Median	MAD	
In-situ Laboratory groundwater well						
pH	pH units	7.00	0.025	7.06	0.12	0.06
EC	µS/cm	9362	37.84	9309	51.46	−52.43
HCO_3^-	mg/L	418.60	17.47	436.26	28.92	17.66
Ca^{2+}	mg/L	369.5	49.5	459.62	31.46	90.11
Mg^{2+}	mg/L	257	9	259.84	25	2.84
Na^+	mg/L	1461	21.5	1460.91	35.045	−0.085
K^+	mg/L	10.5	0.5	12.77	1.21	2.27
Cl^-	mg/L	3202	50.5	3082	198	−120
SO_4^{2-}	mg/L	309	2.5	151	12	−158
Fe^{3+}	µg/L	4486.16	583.95	5881.70	1137.33	1395.54
Mn^{2+}	µg/L	242.54	2.03	261.2	3.22	18.66
Sr^{2+}	µg/L	2959.1	170.47	2800.19	58.98	−158.91
$\delta^{13}C$ CO_2	‰VPDB	−22.14	0.13	−21.96	0.096	0.18
$\delta^{13}C_{(DIC)}$	‰VPDB	−13.14	0.37	−4.71	1.56	8.43

carbonated water during leakage incident into aquifer or due to decomposition of organic matter in aquifer. Long term groundwater monitoring is currently being undertaken to further delineate the observed chemical characteristics.

It is important to note that the groundwater monitoring program does not necessarily indicate containment; it does however provide assurance to the community and regulators that the natural resources have not been impacted by CO_2 activities and can continue to be used safely.

7. Conclusions

As part of In-situ Laboratory project, approximately 38 t of food grade CO_2 were injected into a fault zone at a depth of approximately 340 m in early February 2019. Environmental assurance monitoring was commenced in January 2019. Groundwater levels of the Perth Superficial aquifer have fluctuated during the monitoring period and these fluctuations could be attributed to natural variations occurring in other parts of the aquifer. No impacts from injection of CO_2 into deeper aquifers (Eneabba) on water levels in the Perth Superficial aquifer were observed. Statistical analysis of groundwater chemical characteristics showed no sign of significant changes; however, some anomalies were observed, which could be attributed to the breach of the observation well as well as other surface activities. The surface gas monitoring program commenced on the 16 January 2019 and involved the application of a range of equipment and analytical instrumentation to monitor the concentration and flux of CO_2 emanating from the soil around the Harvey 2 field site.

The results obtained to date can be summarised as follows:

- Groundwater monitoring program reveals no negative physical or chemical impact on the groundwater resources attributable to the CO_2 injection project in the area.
- Elevated levels of CO_2 were detected near the monitoring well for a short period (over several hours) during injection which was the result of the well leakage incident;
- The measured CO_2 soil flux post injection are similar to the baseline levels observed prior to injection. No significant CO_2 leakage has been detected up to two months after injection;
- Parts of the surface monitoring program are ongoing (i.e., Li-COR, West Systems, soil-gas wells) and will continue for a period after the project end date.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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